TABLE I

Oxidant	Millimoles of oxid.	Moles of gas per mole of oxid.	Moles of gas per mole of hydrazine	N_2O in gas, %	Product	Yield, %
Hexyl nitrite	20	1	2	50	Hexanol	>90
Hexyl nitrate	13.6	1.5	1.5	38	Hexanol	>90
Nitrobenzene	20	1.5	1	0	Aniline	100
m-Chloronitrobenzene	20	1.5	1	0	*m*-Chloroaniline	100
m-Dinitrobenzene	20	1.4	0.9	0	*m*-Nitroaniline	75

added and the solution stirred in a nitrogen atmosphere for 30 min. No gas was evolved but the titer of the solution was reduced 10.5% as measured by titration with acid and 11% as measured by titration with iodate.

The reduction of hexyl nitrate and nitrobenzene in the presence of palladium with methylhydrazine was performed in the same manner as the reductions with hydrazine. Both methane and ethane were formed and identified from the infrared spectra of the gases. No ethylene was present. In the reduction of nitrobenzene successive samples taken during one run showed that the ethane band at 6.8 microns became weaker and the methane band at 7.6 microns became stronger as the reaction progressed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Two Stage Polymerizations. I. Preparation and Polymerization of Substituted Allyl Phenyl Ethers[1,2]

BY GEORGE B. BUTLER AND FRANCIS L. INGLEY

Eight new substituted allyl ethers of allyl substituted phenols have been prepared and characterized. These compounds were polymerized under the influence of boron trifluoride to produce thermoplastic polymers containing residual unsaturation indicating that the allyl side chains attached to the ring were not involved in the polymerization. It has been shown that the unsaturated polymers may be copolymerized with drying oils at elevated temperatures.

The industrial importance of two stage polymerizations has been demonstrated in the vulcanization of rubber, and in the thermosetting of phenol–formaldehyde, urea-formaldehyde and alkyd type polymers. More recently Mark[3] has shown that when vinyl *n*-propyl ketone is copolymerized with 10% of vinyl allyl ketone, linear chain-molecules are formed primarily through the more readily polymerized groups only, leaving the less reactive allyl groups intact. More vigorous treatment then results in a cross-linking of the primary chains through the less readily polymerized allyl groups.

The purpose of this investigation was to locate and study other systems which lend themselves to two stage polymerizations.

A review of the literature revealed that little work had been done in connection with the polymerization of allyl phenyl ethers. Related compounds, 2-allylphenol and 2-allylanisole, were converted to polysulfones by Ryden, Glavis and Marvel.[4] These products were prepared by treating the compounds with sulfur dioxide in a pressure bottle, using ascaridole as catalyst. Staudinger and Dreher[5] found that allylbenzene, 4-methoxy- and 4-ethoxyallylbenzene did not undergo polymerization under the influence of boron trifluoride as did the isomeric propenylbenzenes.

Preliminary experiments showed that allyl and 2-methylallyl phenyl ethers would undergo polymerization under the influence of the boron trifluoride–diethyl ether complex. This information in conjunction with Staudinger's experiments with allylbenzenes led us to believe that it would be possible to selectively polymerize allyl ethers of allyl substituted phenols to produce thermoplastic polymers containing residual unsaturated groups. The possibility of further polymerization of polymers of this type under different conditions to produce cross-linked polymers adds to their potential usefulness.

This paper deals with the preparation of several allyl ethers of allyl substituted phenols and polymerization of the compounds with boron trifluoride. The resulting polymers are thermoplastic, indicating that the allyl ether groups undergo polymerization while the allyl side chains of the ring are unaffected.

Attempts to catalyze polymerization of these compounds with benzoyl peroxide, *t*-butyl hydroperoxide and di-*t*-butyl peroxide were unsuccessful. Attempts to copolymerize these compounds with styrene and diallyl maleate, using the above catalysts, were also unsuccessful.

The fact that these compounds, even those containing as many as three unsaturated groups per molecule, do not undergo bulk polymerization as a result of peroxide catalysis is perhaps understandable in the light of the recent work of Erickson.[6] Phenols, which are potential by-products by Claisen rearrangement when allyl phenyl ethers are heated, are known to be polymerization inhibitors.

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(1) Abstracted from a thesis presented by Francis L. Ingley to The Graduate School of the University of Florida in partial fulfillment of the requirements for the M.S. degree, February, 1949.

(2) Presented before the Division of Organic Chemistry at the Atlantic City, N. J., Meeting of the American Chemical Society, Sept., 1949.

(3) Ritchie, "A Chemistry of Plastics and High Polymers," Cleaver-Hume Press, London, 1949, pp. 58–59.

(4) Ryden, Glavis and Marvel, THIS JOURNAL, **59**, 1014 (1937).

(5) Staudinger and Dreher, *Ann.*, **517**, 73 (1939).

(6) Erickson, U. S. Patent 2,455,745.

TABLE I

SUBSTITUTED ALLYL PHENYL ETHERS

Ether	Empirical formula	$n^{25}D$	d^{25}_4	Boiling range °C.	Boiling range Mm.	Yield, %	Chlorine, % Calcd.	Chlorine, % Found
2-Methyllallyl-2-	$C_{13}H_{16}O$	1.5180	0.9485	112.5–113.5	8.0–9.0	63.9	82.93[a,b]	82.90[a]
2-Chloroallyl-2-	$C_{12}H_{13}OCl$	1.5320	1.077	125–128	8.0–9.0	68.4	16.99	16.92
cis-3-Chloroallyl-2-	$C_{12}H_{13}OCl$	1.5369	1.086	83–86	1.0	68.1	16.99	16.95
trans-3-Chloroallyl-2-	$C_{12}H_{13}OCl$	1.5403	1.085	103–106	1.0	58.8	16.99	16.87
2-Chloroallyl-2,6-di-	$C_{15}H_{17}OCl$	1.5297	1.043	108–110	0.7–1.0	81.5	14.25	14.24
2-Methyl allyl-2,6-di-	$C_{16}H_{20}O$	1.5168	0.9371	101–105	0.7–0.9	95.8	84.16[a,c]	84.23[a]
trans-3-Chloroallyl-2,6-di-	$C_{14}H_{17}OCl$	1.5484	1.040	130–135	1.0–2.0	72.7	14.25	14.33
cis-3-Chloroallyl-2,6-di-	$C_{15}H_{17}OCl$	1.5339	1.051	117	0.7–1.0	74.0	14.25	14.31

[a] Carbon, %. [b] Calcd., H, 8.57; found, H, 8.52. [c] Calcd., H, 8.83; found, H, 8.84.

Experimental

Materials.—The allyl halides used in this investigation were products of the Shell Chemical Corporation. The 3-chloropropene-1 was redistilled, the fraction boiling in the range 44.7–45.0°, being used. The 2,3-dichloropropene-1 was fractionated, the fraction distilling between 93 and 95° being taken. The 1,3-dichloropropene-1, a mixture of the *cis* and *trans* isomers, was fractionated. The fraction boiling in the range 103.5–104.5° was considered to be the *cis* isomer and that boiling in the range 112–113°, the *trans* isomer.[7] The 2-methyl-3-chloropropene-1 was used without redistillation.

The 2-allylphenol and 2,6-diallylphenol were prepared by the procedure outlined.[8] Reagent grade potassium carbonate, potassium iodide and potassium hydroxide were used. The methyl ethyl ketone was a product of Shell Chemical Corporation, and the boron trifluoride–diethyl ether complex (technical grade) a product of Baker and Adamson.

Preparation of Ethers of 2-Allylphenol.—Mauthner's[9] modification of the method originally employed by Claisen and Eisleb[10] for the preparation of allyl phenyl ethers was used, with slight modifications, for the preparation of ethers of 2-allylphenol. The modifications involved the use of a higher boiling ketone, methyl ethyl ketone, as solvent and refluxing periods of ten hours to insure more complete reaction. The products were purified by fractionation through a 2 × 28 cm. column packed with small glass helices.

Preparation of Ethers of 2,6-Diallylphenol.—Ethers of this phenol were prepared by making use of the modification reported by Tarbell and Wilson[11] in which they found that substitution of sodium hydroxide for potassium carbonate resulted in better yields of ethers of weakly acidic phenols. Methyl ethyl ketone was used as solvent and refluxing periods as long as 24 hours were found to be necessary for complete reaction. The products were purified as previously described.

The physical properties and analyses of these compounds are recorded in Table I.

Polymerization Studies.—One gram of the compound to be polymerized was placed in a small test-tube with a thermometer inserted. Five drops (0.1 g.) of the boron trifluoride–diethyl ether complex were added dropwise, and the temperature change was observed. If no change of temperature occurred, the tube was heated very slowly until evidence of an exothermic reaction occurred. At this time, heating was discontinued and the initial temperature of the reaction recorded. After the reaction had subsided and the polymer had cooled, it was finely ground, when solid, and washed thoroughly with water and dried. The polymers obtained by this method were generally dark before washing. With the exception of those polymers obtained from the 2-chloroallyl ethers which were viscous liquids, all were brittle solids. All of the polymers were found to be thermoplastic, soluble in xylene and insoluble in water, and having melting points in the range of 35–80°.

In order to determine whether or not the catalyst caused cleavage of the ether linkage, 15 g. of 2-methylallyl 2-allylphenyl ether was polymerized by heating on a steam-bath in presence of 22 drops (0.4 g.) of the boron trifluoride–diethyl ether complex for 6 hours and at 110° for an additional period of 4 hours. The polymer obtained weighed 15 g., indicating that no decomposition had occurred and that no part of the original molecule was lost. *Anal.* of the polymer: Calcd. for $(C_{13}H_{16}O)_n$: C, 82.93; H, 8.57. Found: C, 82.35; H, 8.54.

Although these polymers were found to be reluctant to undergo thermosetting as the result of peroxide catalysis, the residual unsaturation was shown to be present through their ability to undergo thermal copolymerization with linseed oil. Forty parts of the thermoplastic polymer prepared by polymerizing allyl 2-allylphenyl ether by the above procedure was dissolved in sixty parts of boiled linseed oil having a viscosity of 0.65 poise, at 25°. The solution was then heated to 300°. After one-half hour at this temperature, it was apparent that gelation had begun. After one hour, gelation was complete. A similar experiment was conducted in which one hundred parts of linseed oil was heated at 300° for an equivalent time with little change in viscosity. Bodied linseed oil having a viscosity of 4.35 poises at 25° when heated alone at 307° requires 235 minutes to reach a viscosity of 148 poises at 25°.[12]

The above results are evidence that the residual unsaturated linkages in the polymer have copolymerized with the double bonds of the drying oil to produce a cross-linked copolymer. If further polymerization of the polymer alone had occurred, an oil insoluble polymer would have resulted.

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[7] Hatch and Perry, THIS JOURNAL, **71**, 3262 (1949).

[8] Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 26.

[9] Mauthner, *J. prakt. Chem.*, [2] **148**, 95 (1937).

[10] Claisen and Eisleb, *Ann.*, **401**, 21–119 (1913).

[11] Tarbell and Wilson, THIS JOURNAL, **64**, 1066 (1942).

[12] "Modern Plastics Encyclopedia," Plastics Catalogue Corporation, New York, N. Y., 1946, p. 1198.

[13] Original manuscript received September 16, 1949.